Silica sulfuric acid promoted selective oxidation of sulfides to sulfoxides or sulfones in the presence of aqueous H_2O_2

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Abstract

Alkyl and aryl sulfides are oxidized to the corresponding sulfoxides or sulfones in excellent yields with aqueous hydrogen peroxide in the presence of silica sulfuric acid as an efficient solid acid catalyst. The oxidation of alkyl and aryl sulfide proceeds at 25–90°C and the corresponding sulfoxides or sulfones was selectively obtained by controlling the amounts of H_2O_2 and catalyst.
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1. Introduction

Organosulfur compounds, such as sulfoxides and sulfones, are useful synthetic reagents in organic chemistry. In particular, sulfoxides are valuable synthetic intermediates for the production of a range of chemically and biologically active molecules including therapeutic agents such as anti-ulcer (proton pump inhibitors), antibacterial, antifungal, anti-atherosclerotic, antihypertensive and cardiotonic agents as well as psychotropics and vasodilators [1–11]. The oxidation of sulfides and utilization of sulfoxides has been reviewed recently [12]. Many reagents are available for the oxidation of sulfides, but most of them are conventional oxidants, which are not suitable for medium to large scale synthesis.
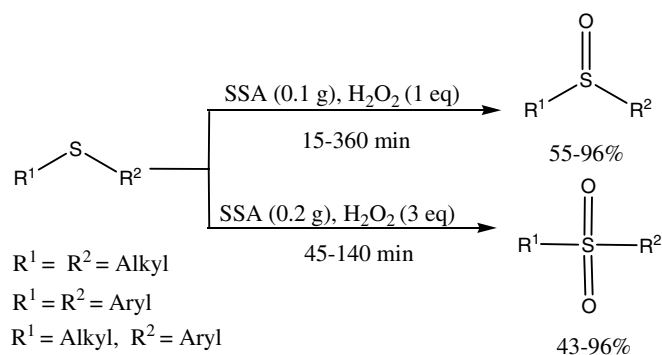
Aqueous H_2O_2 is an ideal oxidant in view of an effective–oxygen content (47%), cleanness that produces only harmless water by reaction [13], safety in storage and operation and the low cost of production transportation [14,15]. Due to the low standard redox potential of H_2O_2 in neutral or weak acidic media, It has been usually used in the presence of strong inorganic acid such as H_2SO_4 [16], HCl [17,18], $HClO_4$ [19], CH_3CO_2H [20] and $H_2Mo_2O_7$ [21]. However, in spite of their potential utility, these homogenous catalyst present limitations due to the use of toxic and corrosive reagents, the tedious work-up procedure, the necessity of neutralization of the strong acidic media, producing undesired washes and long reaction times. Furthermore, in these types of reactions which the catalyst dissolved in organic phase inherently require separation of the catalyst from the product and invariably a chromatographic procedure for recovery of the catalyst [22].

Recently, a number of transition metal (Ti, Mo, Fe, V, W, Re, Ru, Sc, Zr and Mn) compounds have been used as catalyst for the selective oxidation of sulfides with H_2O_2 [23–32]. However, one of the problems frequently encountered in metal-catalyzed oxidation with H_2O_2 is the concomitant decomposition of H_2O_2, which makes the use of a large excess of H_2O_2 necessary to reach full conversion. For example, the oxidation of various sulfides to sulfones by H_2O_2 mediated in the presence of $TiCl_3$ or $ZrCl_4$ was employed 7–10 fold excess H_2O_2 and 2 equivalents of $TiCl_3$ or $ZrCl_4$ per mole of sulfides [31,32]. In addition, there are several disadvantages for those methods such as: using toxic transition metal compounds, preparation of complex catalyst, removing or recovery of the expensive catalyst and remaining metals in products.

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Scheme 1.

During the course of our studies on the development of new routes for the oxidation of organic compounds [33a,b,c,d], we now report the selective oxidation of sulfides to sulfoxides or sulfones with H_2O_2 in the presence of silica sulfuric acid (SSA) [34] as a solid acid promoter by controlling the amounts of H_2O_2 and SSA (Scheme 1).

2. Experimental

2.1. General

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a shimadzu IR-470 spectrometer. ^{1}H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz in CDCl$_3$. GC chromatogram was recorded by Varian 3600 CP apparatus.

2.2. Typical experimental procedure for the preparation of sulfoxides

In a 25 ml round bottom flask, to a solution of sulfide (1 mmol) in CH$_3$CN (5 ml), 30% (w/w) H$_2$O$_2$ (1 equivalent) and the SSA catalyst (0.1 g) was added successively and the mixture was stirred magnetically at room temperature for the indicated time in Table 1. The progress of the reaction

Table 1
The yield and selectivity as a function of time in the oxidation of dibenzyl phenyl sulfide to the corresponding sulfoxide or sulfone with aqueous hydrogen peroxide in the presence of SSA

Time (min)	Conversion of sulfide[a] to: (%)		Conversion of sulfide[b] to: (%)	
	Sulfoxide	Sulfone	Sulfoxide	Sulfone
10	70	Trace	Trace	50
20	90	7	Trace	60
40			5	70
60			5	80
80			Trace	90
90			0	94

[a] Dibenzyl phenyl sulfide (1 mmol), hydrogen peroxide (1 eq) and SSA (0.1 g).
[b] Dibenzyl phenyl sulfide (1 mmol), hydrogen peroxide (3 eq) and SSA (0.2 g).

Table 2
Oxidation of sulfides (1 mmol) to sulfoxides by H$_2$O$_2$ (1 eq) in the presence of SSA (0.1 g) at room temperature in CH$_3$CN

Entry	Substrate	Product	Yield (%)/ time (min)	Mp or Bp (°C) found (reported)
1			92/30	31–33 (30–30.5)[a]
2			95/360	69–72 (72–73)[a]
3			89/35	142–144 (138–140)[b]
4			83/60	132–135 (136–137)[b]
5			87/80	72–75 (74–76)[c]
6			92/75	143–145 (140–142)[b]
7			85/15	142–145 (146)[c]
8			96/40	42–44 (43–45)[c]
9			93/15	132–134 (133–135)[c]
10			91/240	149–152 (153–155)[b]
11			72/60	103–105 (103–106)[d]
12			55/30	24–26 (24.5–25.5)[e]
13			60/30	29–32 (29–32)[a]

[a] Ref. [37].
[b] Ref. [38].
[c] Ref. [39].
[d] Ref. [40].
[e] Ref. [41].

Table 3
Oxidation of sulfides (1 mmol) to sulfones with H_2O_2 (3 eq) in the presence of SSA (0.2 g) at room temperature in CH_3CN

Entry	Substrate	Product	Yield (%)/ time (min)	Mp or Bp (°C) found (reported)
1	Ph–S–CH$_3$	Ph–SO$_2$–CH$_3$	96/ 45	85–87 (89–90)[a]
2[b]	Ph–S–Ph	Ph–SO$_2$–Ph	95/ 45	126–128 (128–129)[a]
3	4-CH$_3$-C$_6$H$_4$–S–CH$_3$	4-CH$_3$-C$_6$H$_4$–SO$_2$–CH$_3$	92/ 60	85–88 (88)[c]
4	4-Cl-C$_6$H$_4$–S–CH$_3$	4-Cl-C$_6$H$_4$–SO$_2$–CH$_3$	90/ 75	95–97 (–)
5	4-Br-C$_6$H$_4$–S–CH$_3$	4-Br-C$_6$H$_4$–SO$_2$–CH$_3$	88/ 100	42–44 (43–44)[d]
6	4-O$_2$N-C$_6$H$_4$–S–CH$_3$	4-O$_2$N-C$_6$H$_4$–SO$_2$–CH$_3$	88/ 140	140–143 (142)[c]
7	PhCH$_2$–S–Ph	PhCH$_2$–SO$_2$–Ph	90/ 75	142–144 (144–145)[e]
8	PhCH$_2$–S–CH$_2$Ph	PhCH$_2$–SO$_2$–CH$_2$Ph	94/ 80	148–151 (149–153)[f]
9	Et–S–Et	Et–SO$_2$–Et	62/ 120	70–73 (73–75)[e]
10	Pr–S–Pr	Pr–SO$_2$–Pr	43/ 50	29–30 (29–30)[e]
11	Bu–S–Bu	Bu–SO$_2$–Bu	100/ 45	43–45 (46–46.5)[a]
12	PhCH$_2$–S(O)–Ph	PhCH$_2$–SO$_2$–Ph	90/ 85	142–144 (144–145)[e]
13	PhCH$_2$–S(O)–CH$_2$Ph	PhCH$_2$–SO$_2$–CH$_2$Ph	91/ 80	148–151 (149–153)[f]

[a] Ref. [37].
[b] The reaction was carried out at 90 °C.
[c] Ref. [42].
[d] Ref. [38].
[e] Ref. [33b].
[f] Ref. [43].

was monitored by TLC or GC. After completion of the reaction, the reaction mixture was filtered and the excess of solvent was removed under reduced pressure to give the corresponding pure sulfoxide (Table 2). All reaction products were known and characterized by IR and ^{1}H NMR spectra and melting point as comparing with those obtained from authentic samples.

2.3. Typical experimental procedure for the preparation of sulfones

In a 25 ml round bottom flask, to a solution of sulfide (1 mmol) in CH_3CN (5 ml), 30% (w/w) H_2O_2 (3 equivalents) and the SSA catalyst (0.2 g) was added successively and the mixture was stirred magnetically at room temperature for the indicated time in Table 2. The progress of the reaction was monitored by TLC or GC. After completion of the reaction, the reaction mixture was filtered and the excess of solvent was removed under reduced pressure to give the corresponding pure sulfones (Table 3). All of the products are known and characterized by IR and ^{1}H NMR spectra and melting point as comparing with those obtained from authentic samples.
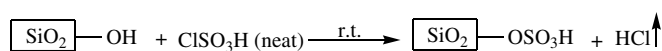
3. Results and discussion

The SSA catalyst is simply prepared by the reaction of chlorosulfonic acid with commercially available silica and the by-product, HCl gas is easily removed from the reaction vessel [34] (Scheme 2).
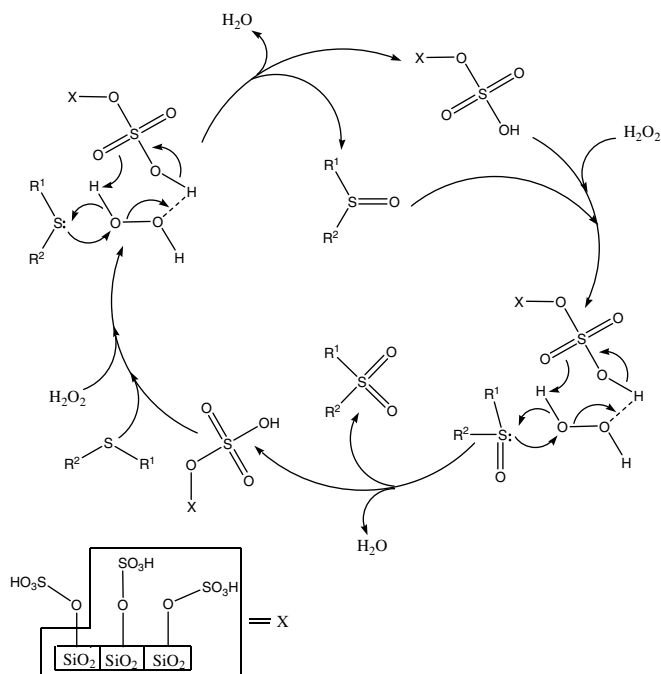
Silica sulfuric acid catalyst provides a valuable tool for the synthesis of both aliphatic and aromatic sulfoxides and sulfones. The optimum ratio of sulfide to H_2O_2 (1:1 equivalent) in the presence of SSA (0.1 g) is found to be ideal for complete conversion of sulfides to sulfoxide (with a few amount of sulfone), which the reaction remains incomplete with lesser amounts. The use of excess reagent (the molar ratio sulfide to H_2O_2 1:3 equivalents in the presence of SSA (0.2 g)) affords the corresponding sulfone in a clean reaction. The yield and selectivity of oxidation dibenzyl phenyl sulfide to the corresponding sulfoxide or sulfone as a function of time is indicated in Table 1.

The generality of this approach has been demonstrated by a facile and effortless oxidant of a wide variety of alkyl, aryl and aromatic sulfides as shown in Tables 2 and 3.

Observation of oxidation benzyl phenyl sulfide and dibenzyl sulfide to the corresponding sulfoxide (Entries 8 and 9 in Table 2) or sulfone (Entries 7 and 8 in Table 3) indicates that the reaction proceeds by way of an oxygen transfer mechanism. If the reaction involved electron transfer instead of oxygen transfer, substantial amounts of benzal-

$$SiO_2\text{—}OH + ClSO_3H \text{ (neat)} \xrightarrow{\text{r.t.}} SiO_2\text{—}OSO_3H + HCl\uparrow$$

Scheme 2.

Scheme 3. Proposed mechanism for the oxidation of sulfide to the corresponding sulfoxide or sulfone with aqueous hydrogen peroxide in the presence of SSA.

dehyde would have been formed [35,36]. Thus, we examined the possibility of the oxidation of sulfoxide to sulfones with H_2O_2/SSA in CH_3CN at room temperature. As indicated in Table 3, both benzyl phenyl sulfoxide and dibenzyl sulfoxide are easily oxidized to the corresponding sulfone after about 80–85 min (Entries 12 and 13). This result confirms that the oxidation of sulfide to sulfone proceeds via the sulfoxide intermediate. The possible mechanism for the oxidation of sulfide to the corresponding sulfoxide or sulfone using H_2O_2 in the presence of SSA is outlined in Scheme 3.

4. Conclusion

In summary, we have shown that the silica based solid acid catalyst, which can be easily prepared from commercially available starting material, efficiently catalyze the selectively synthesis of sulfoxide or sulfone by the oxidation of sulfide by aqueous hydrogen peroxide at room temperature. Due to the environmental friendly behavior of SSA with respect to corrosiveness, safety, waste and ease of separation of SSA, replacement of liquid acids and expensive toxic transition metal compounds with SSA are desirable in the oxidation of sulfides to the corresponding sulfoxide or sulfone in chemical industry.

Acknowledgements

References

[1] E.N. Prilezhaeva, Russ. Chem. Rev. 70 (2001) 897.
[2] M.C. Carreno, Chem. Rev. 95 (1995) 1717.
[3] M. Sovova, P. Sova, Ceska Slov. Farm. 52 (2003) 82.
[4] B. Kotelanski, R.J. Grozmann, J.N.C. Cohn, Pharmacol. Ther. 14 (1973) 427.
[5] I. Fernandez, N. Khiar, Chem. Rev. 103 (2003) 3651.
[6] A. Thorarensen, A. Palmgren, K. Itami, J.E. Backvall, Tetrahedron Lett. 38 (1997) 8541.
[7] A.V. Nieves, A.E. Lang, Clin. Neuropharmacol. 25 (2002) 111.
[8] S. Padmanabhan, R.C. Lavin, G.J. Durant, Tetrahedron: Asymmetry 11 (2000) 3455.
[9] J.G. Rowlands, Synlett (2003) 236.
[10] R. Dorta, L.J.W. Shimon, D. Milstein, Chem. Eur. J. 9 (2003) 5237.
[11] A.M. Khenkin, R. Neumann, J. Am. Chem. Soc. 124 (2002) 4198.
[12] K. Kaczorowska, Z. kolarska, K. Mitka, P. Kowalski, Tetrahedron 61 (2005) 8315.
[13] K. Sato, M. Aoki, R. Noyori, Science 281 (1998) 1646.
[14] C.W. Jones, Applications of Hydrogen Peroxide and Derivatives, Royal Society of Chemistry, Cambridge, 1999.
[15] G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic Publishers, Dordrecht, 1992.
[16] V.P. Tutubalina, Khim. Tekhnol. Pererab. Nefti Gaza 28 (1982); Chem. Abstr. 99 (1983) 25144g.
[17] V.P. Krivonogov, R.M. Shayakhmetova, V.I. Dronov, R.S. Enikeev, Y.E. Nikitin, N.L. Egutkin, A.S. Bodrova, L.V. Spirikhin, Zh. Prikl. Khim. 54 (1981) 2505; Chem. Abstr. 96 (1981) 67897y.
[18] H. Firouzabadi, N. Iranpoor, A.A. Jafari, E. Riazymontazer, Adv. Synth. Catal. 348 (2006) 434.
[19] A.C. Chatterji, Z. Roy, Phys. Chem. (Leipzig) 250 (1972) 137; Chem. Abstr. 77 (1972) 139201z.
[20] F. Hosseinpoor, H. Golchoubian, Tetrahedron Lett. 47 (2006) 5195.
[21] H.B. Freyermuth, H.S. Schultz, S.R. Buc, US Patent 3,005,852, (1959); Chem. Abstr. 56 (1962) 4679b.
[22] (a) G.J. Ten-Brink, I.W.C.E. Arends, R.A. Shelden, Adv. Synth. Catal. 344 (2002) 355; (b) G.J. Ten-Brink, I.W.C.E. Arends, R.A. Shelden, Science 287 (2000) 1636.
[23] O. Bortolini, F. Difuria, G. Modena, R. Seraglia, J. Org. Chem. 50 (1985) 2688.
[24] A. Massa, E.M. De Lorenzo, A. Scettri, J. Mol. Cata. A 250 (2006) 27.
[25] K. Jeyakumar, D.K. Chand, Tetrahedron Lett. 47 (2006) 4573.
[26] I. Khedher, A. Ghorbel, J.M. Fraile, J.A. Mayoral, J. Mol. Cata. A 255 (2006) 92.
[27] M.R. Berenguer, P.J. Campon, L. Coppi, EP Patent 1,270,555A1; Chem. Abstr. 135 (2003) 242230.
[28] J. Oguma, K. Hagiya, T. Miyawaki, EP Patent 1,334,956A2; Chem. Abstr. 136 (2002) 164701.
[29] H. Hashimoto, T. Urai, EP Patent 1,277,752A1; Chem. Abstr. 135 (2003) 357923.
[30] H. Cotton, WO Patent 9,925,711; Chem. Abstr. 131 (2000) 5258y.
[31] Y. Watanabe, T. Numata, S. Oae, Synthesis (1981) 204.
[32] K. Bahrami, Tetrahedron Lett. 47 (2006) 2009.
[33] (a) A. Shaabani, S. Naderi, A. Rahmati, Z. Badri, M. Darvishi, D.G. Lee, Synthesis (2005) 3023; (b) A. Shaabani, P. Mirzaei, S. Naderi, D.G. Lee, Tetrahedron 60 (2004) 11415;

(c) A. Shaabani, A. Bazgir, F. Teimouri, D.G. Lee, Tetrahedron Lett. 43 (2002) 5165;

(d) A. Shaabani, D.G. Lee, Tetrahedron Lett. 42 (2001) 5833.

[34] M.A. Zolfigol, Tetrahedron 57 (2001) 9509.

[35] E. Baciocchi, O. Lanzalunga, S. Malandrucco, J. Am. Chem. Soc. 118 (1996) 8973.

[36] E. Baciocchi, O. Lanzalunga, B. Pirozzi, Tetrahedron 53 (1997) 12287.

[37] K. Sato, M. Hyodo, M. Aoki, X.Q. Zheng, R. Noyori, Tetrahedron 57 (2001) 2469.

[38] The Sadtler Standard Spectra, NMR, Sadtler Research Laboratories, INC, 12327M (1972).;
Chem. Abstr. 52 (1958) 4543.

[39] Dictionary of Organic Compounds, sixth ed., Chapman and Hall, London, 1996.

[40] Handbook of Chemistry and Physics, 70th ed., CRC Press, 1989-1990.

[41] S.J. Searles, H.Y. Hays, J. Org. Chem. 23 (1958) 2028.

[42] S. Rozen, Y. Bareket, J. Org. Chem. 62 (1997) 1457.

[43] H. Rheinboldt, E. Giesbrecht, J. Am. Chem. Soc. 68 (1964) 973.